

1                                   **HYDROCARBON CONVERSION USING**  
2                                   **MOLECULAR SIEVE SSZ-51**

3  
4                                   **FIELD OF INVENTION**

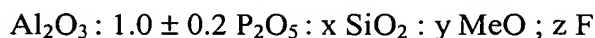
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6           The present invention relates in general to crystalline aluminophosphate  
7 compositions, and more particularly to novel crystalline aluminophosphates and  
8 metalloaluminophosphates of the molecular sieve type, methods of its preparation and  
9 their use in catalysts for, e.g., hydrocarbon conversion reactions.

10  
11                               **BACKGROUND OF THE INVENTION**

12  
13           Microporous crystalline aluminophosphate compositions having open  
14 framework structures formed of  $\text{AlO}_2$  and  $\text{PO}_2$  tetrahedral units joined by the sharing  
15 of the corner oxygen atoms and characterized by having pore openings of uniform  
16 dimensions have heretofore been disclosed in a number of publications, notably the  
17 specification of U.S. Pat. No. 4,310,440 issued July 7, 1980, to S. T. Wilson et al.  
18 The Wilson et al. aluminophosphates constitute a generic class of non-zeolitic  
19 molecular sieve materials which are capable of undergoing complete and reversible  
20 dehydration while retaining the same essential framework topology in both the  
21 anhydrous and hydrated state. By the term "essential framework topology" or  
22 "essential framework structure" as used in the aforesaid patent, and also in the present  
23 specification and claims, is meant the spatial arrangement of the primary Al-O and P-  
24 O bond linkages. Other microporous aluminophosphates which undergo structure  
25 rearrangements, either reversibly or irreversibly, upon partial or complete dehydration  
26 are also known, for example the minerals variscite and metavariscite and certain of  
27 the synthetic metastable aluminophosphates reported by F. D'Yvoire [Bull. Soc.  
28 Chim. France, 1762 (1961)]. Another class of synthetic crystalline compositions  
29 contains framework tetrahedral metal oxides of manganese, magnesium, cobalt,  
30 and/or zinc in addition the  $\text{AlO}_2$  and  $\text{PO}_2$  tetrahedra. These are sometimes termed  
31 metalloaluminophosphates or MAPO'S.

## SUMMARY OF THE INVENTION

The present invention provides a novel microporous crystalline aluminophosphates ("ALPO's"), aluminosilicophosphates ("APSO's"), metalloaluminophosphates ("MAPO's") and metalloaluminosilicophosphates ("MAPSO's") denominated SSZ-51 and the methods for its preparation. SSZ-51 has an essential framework structure whose chemical composition, expressed in terms of mole ratios after calcination, is:



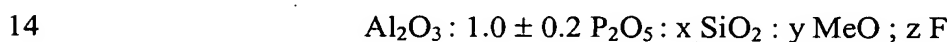
where x has a value of 0 to 0.2 and y has a value of 0 to 0.2, z has a value of 0 to 0.10 and Me represents at least one element, other than aluminum, phosphorus or silicon, which is capable of forming an oxide in coordination with (AlO<sub>2</sub>) and (PO<sub>2</sub>) oxide structural units in the molecular sieve (such as a divalent metal). After calcination and in the hydrated state, SSZ-51 exhibits an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table II set forth hereinafter.

The framework structure of SSZ-51 consists of a building unit which is essentially a double four ring (D4R) with one disconnected (or ring-opened) edge. The fluoride ion used in synthesizing SSZ-51 is encapsulated within this building unit and forms a bridge between two of the aluminum atoms. Each building unit is then connected to four other identical building units, through two Al-O-P linkages per unit. These building units can be linked together to form the two structures, the SSZ-51 structure of this invention and a material having the structure designated AFR (e.g., SAPO-40). The building units can be joined in a "head-to-tail" fashion to form chains running parallel to the c-direction. Chains are linked together through four-rings to form undulating layers. The orientation of successive chains in these layers is anti-parallel. This layer is a building block of both SSZ-51 and AFR. The undulating layers can be linked in two ways. If the layers are linked so that there is inversion symmetry between the layers, this results in the SSZ-51 structure. If the layers are linked so that there is "mirror" symmetry between the layers the resulting structure is that of AFR (mirror symmetry here refers to the framework, i.e., excludes the need for Al/P ordering).

1       SSZ-51 can be prepared by hydrothermal crystallization from a reaction mixture  
2 containing in addition to water, a reactive source of aluminum, phosphorus and  
3 fluoride and an organic templating agent (sometimes referred to as a structure  
4 directing agent or "SDA") which is 4-dimethylaminopyridine. Thus, the present  
5 invention further provides a method of preparing a crystalline material comprising  
6 contacting under crystallization conditions a reaction mixture comprising a reactive  
7 source of aluminum, a reactive source of phosphorus, a reactive source of fluoride and  
8 an organic templating agent comprising 4-dimethylaminopyridine. The reaction  
9 mixture may further comprise a reactive source of a metal selected from the group  
10 consisting of magnesium, manganese, cobalt, zinc and nickel.

11       Thus, the present invention provides a molecular sieve whose chemical  
12 composition, expressed in terms of mole ratios of oxides after calcination, is:

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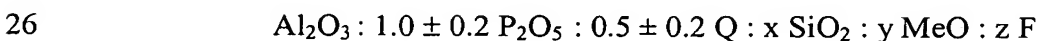
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16 where x has a value of 0 to 0.2, y has a value of 0 to 0.2, z has a value of 0 to 0.10 and  
17 Me represents at least one element, other than aluminum, phosphorus or silicon,  
18 which is capable of forming an oxide in coordination with (AlO<sub>2</sub>) and (PO<sub>2</sub>) oxide  
19 structural units in the molecular sieve, the molecular sieve having, after calcination  
20 and in the hydrated state, the X-ray diffraction lines of Table II.

21       The present invention further provides such a molecular sieve wherein Me is  
22 selected from the group consisting of magnesium, manganese, cobalt, zinc and nickel.

23       Further provided by the present invention is a molecular sieve composition, as-  
24 synthesized, whose general formula, in terms of mole ratios, is as follows:

25



27

28 where x has a value of 0 to 0.2, y has a value of 0 to 0.2, Q is 4-  
29 dimethylaminopyridine, z has a value of 0.02 to 0.50 and Me represents at least one  
30 element, other than aluminum, phosphorus or silicon, which is capable of forming an  
31 oxide in coordination with (AlO<sub>2</sub>) and (PO<sub>2</sub>) oxide structural units in the molecular  
32 sieve.

1       The present invention also provides such an as-synthesized molecular sieve  
2 wherein Me is selected from the group consisting of magnesium, manganese, cobalt,  
3 zinc and nickel.

4       Also provided by the present invention is such an as-synthesized molecular  
5 sieve having, in an anhydrous state, the X-ray diffraction lines of Table I.

6       In accordance with the present invention there is provided a process for  
7 converting hydrocarbons comprising contacting a hydrocarbonaceous feed at  
8 hydrocarbon converting conditions with a catalyst comprising the molecular sieve of  
9 this invention. The molecular sieve may be predominantly in the hydrogen form. It  
10 may also be substantially free of acidity.

11       Further provided by the present invention is a hydrocracking process  
12 comprising contacting a hydrocarbon feedstock under hydrocracking conditions with  
13 a catalyst comprising the molecular sieve of this invention, preferably predominantly  
14 in the hydrogen form.

15       This invention also includes a dewaxing process comprising contacting a  
16 hydrocarbon feedstock under dewaxing conditions with a catalyst comprising the  
17 molecular sieve of this invention, preferably predominantly in the hydrogen form.

18       The present invention also includes a process for improving the viscosity  
19 index of a dewaxed product of waxy hydrocarbon feeds comprising contacting the  
20 waxy hydrocarbon feed under isomerization dewaxing conditions with a catalyst  
21 comprising the molecular sieve of this invention, preferably predominantly in the  
22 hydrogen form.

23       The present invention further includes a process for producing a C<sub>20+</sub> lube oil  
24 from a C<sub>20+</sub> olefin feed comprising isomerizing said olefin feed under isomerization  
25 conditions over a catalyst comprising the molecular sieve of this invention. The  
26 molecular sieve may be predominantly in the hydrogen form. The catalyst may  
27 contain at least one Group VIII metal.

28       In accordance with this invention, there is also provided a process for  
29 catalytically dewaxing a hydrocarbon oil feedstock boiling above about 350°F  
30 (177°C) and containing straight chain and slightly branched chain hydrocarbons  
31 comprising contacting said hydrocarbon oil feedstock in the presence of added  
32 hydrogen gas at a hydrogen pressure of about 15-3000 psi (0.103 – 20.7 MPa) with a  
33 catalyst comprising the molecular sieve of this invention, preferably predominantly in

1 the hydrogen form. The catalyst may contain at least one Group VIII metal. The  
2 catalyst may be a layered catalyst comprising a first layer comprising the molecular  
3 sieve of this invention, and a second layer comprising an aluminosilicate molecular  
4 sieve which is more shape selective than the molecular sieve of said first layer. The  
5 first layer may contain at least one Group VIII metal.

6 Also included in the present invention is a process for preparing a lubricating  
7 oil which comprises hydrocracking in a hydrocracking zone a hydrocarbonaceous  
8 feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically  
9 dewaxing said effluent comprising hydrocracked oil at a temperature of at least about  
10 400°F (204°C) and at a pressure of from about 15 psig to about 3000 psig (0.103 –  
11 20.7 Mpa gauge) in the presence of added hydrogen gas with a catalyst comprising the  
12 molecular sieve of this invention. The molecular sieve may be predominantly in the  
13 hydrogen form. The catalyst may contain at least one Group VIII metal.

14 Further included in this invention is a process for isomerization dewaxing a  
15 raffinate comprising contacting said raffinate in the presence of added hydrogen with  
16 a catalyst comprising the molecular sieve of this invention. The raffinate may be  
17 bright stock, and the molecular sieve may be predominantly in the hydrogen form.  
18 The catalyst may contain at least one Group VIII metal.

19 Also included in this invention is a process for increasing the octane of a  
20 hydrocarbon feedstock to produce a product having an increased aromatics content  
21 comprising contacting a hydrocarbonaceous feedstock which comprises normal and  
22 slightly branched hydrocarbons having a boiling range above about 40°C and less  
23 than about 200°C, under aromatic conversion conditions with a catalyst comprising  
24 the molecular sieve of this invention made substantially free of acidity by neutralizing  
25 said molecular sieve with a basic metal. Also provided in this invention is such a  
26 process wherein the molecular sieve contains a Group VIII metal component.

27 Also provided by the present invention is a catalytic cracking process  
28 comprising contacting a hydrocarbon feedstock in a reaction zone under catalytic  
29 cracking conditions in the absence of added hydrogen with a catalyst comprising the  
30 molecular sieve of this invention, preferably predominantly in the hydrogen form.  
31 Also included in this invention is such a catalytic cracking process wherein the  
32 catalyst additionally comprises a large pore crystalline cracking component.

33 This invention further provides an isomerization process for isomerizing C<sub>4</sub> to

1 C<sub>7</sub> hydrocarbons, comprising contacting a feed having normal and slightly branched  
2 C<sub>4</sub> to C<sub>7</sub> hydrocarbons under isomerizing conditions with a catalyst comprising the  
3 molecular sieve of this invention, preferably predominantly in the hydrogen form.  
4 The molecular sieve may be impregnated with at least one Group VIII metal,  
5 preferably platinum. The catalyst may be calcined in a steam/air mixture at an  
6 elevated temperature after impregnation of the Group VIII metal.

7 Also provided by the present invention is a process for alkylating an aromatic  
8 hydrocarbon which comprises contacting under alkylation conditions at least a molar  
9 excess of an aromatic hydrocarbon with a C<sub>2</sub> to C<sub>20</sub> olefin under at least partial liquid  
10 phase conditions and in the presence of a catalyst comprising the molecular sieve of  
11 this invention, preferably predominantly in the hydrogen form. The olefin may be a  
12 C<sub>2</sub> to C<sub>4</sub> olefin, and the aromatic hydrocarbon and olefin may be present in a molar  
13 ratio of about 4:1 to about 20:1, respectively. The aromatic hydrocarbon may be  
14 selected from the group consisting of benzene, toluene, ethylbenzene, xylene,  
15 naphthalene, naphthalene derivatives, dimethylnaphthalene or mixtures thereof.

16 The present invention also provides a process for alkylating an aromatic  
17 hydrocarbon which comprises contacting under alkylation conditions an aromatic  
18 hydrocarbon with a C<sub>20+</sub> olefin under at least partial liquid phase conditions and in the  
19 presence of a catalyst comprising the molecular sieve of this invention, preferably  
20 predominantly in the hydrogen form. The aromatic hydrocarbon and olefin are  
21 present in a molar ratio of about 1:15 to about 25:1, respectively. The aromatic  
22 hydrocarbon is selected from the group consisting of benzene, toluene, ethylbenzene,  
23 xylene, naphthalene, naphthalene derivatives, dimethylnaphthalene or mixtures  
24 thereof.

25 Further provided in accordance with this invention is a process for  
26 transalkylating an aromatic hydrocarbon which comprises contacting under  
27 transalkylating conditions an aromatic hydrocarbon with a polyalkyl aromatic  
28 hydrocarbon under at least partial liquid phase conditions and in the presence of a  
29 catalyst comprising the molecular sieve of this invention, preferably predominantly in  
30 the hydrogen form. The aromatic hydrocarbon and the polyalkyl aromatic  
31 hydrocarbon may be present in a molar ratio of from about 1:1 to about 25:1,  
32 respectively.

33 The aromatic hydrocarbon may be selected from the group consisting of  
34 benzene, toluene, ethylbenzene, xylene, or mixtures thereof, and the polyalkyl

1 aromatic hydrocarbon may be a dialkylbenzene.

2 Further provided by this invention is a process to convert paraffins to  
3 aromatics which comprises contacting paraffins under conditions which cause  
4 paraffins to convert to aromatics with a catalyst comprising the molecular sieve of this  
5 invention; said catalyst comprising gallium, zinc, or a compound of gallium or zinc.

6 In accordance with this invention there is also provided a process for  
7 isomerizing olefins comprising contacting said olefin under conditions which cause  
8 isomerization of the olefin with a catalyst comprising the molecular sieve of this  
9 invention.

10 Further provided in accordance with this invention is a process for isomerizing  
11 an isomerization feed comprising an aromatic C<sub>8</sub> stream of xylene isomers or  
12 mixtures of xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio  
13 of ortho-, meta- and para-xylenes is obtained, said process comprising contacting said  
14 feed under isomerization conditions with a catalyst comprising the molecular sieve of  
15 this invention.

16 The present invention further provides a process for oligomerizing olefins  
17 comprising contacting an olefin feed under oligomerization conditions with a catalyst  
18 comprising the molecular sieve of this invention.

19 This invention also provides a process for converting oxygenated  
20 hydrocarbons comprising contacting said oxygenated hydrocarbon with a catalyst  
21 comprising the molecular sieve of this invention under conditions to produce liquid  
22 products. The oxygenated hydrocarbon may be a lower alcohol.

23 Further provided in accordance with the present invention is a process for the  
24 production of higher molecular weight hydrocarbons from lower molecular weight  
25 hydrocarbons comprising the steps of:

26 (a) introducing into a reaction zone a lower molecular weight hydrocarbon-  
27 containing gas and contacting said gas in said zone under C<sub>2+</sub> hydrocarbon  
28 synthesis conditions with the catalyst and a metal or metal compound capable of  
29 converting the lower molecular weight hydrocarbon to a higher molecular  
30 weight hydrocarbon; and

31 (b) withdrawing from said reaction zone a higher molecular weight  
32 hydrocarbon-containing stream.

33  
34

1 BRIEF DESCRIPTION OF THE FIGURES

2  
3 Figure 1 is an X-ray pattern (CuK $\alpha$ ) of calcined and hydrated SSZ-51.

4 Figure 2 is a series of X-ray patterns (synchrotron, 0.704 Angstrom)  
5 illustrating the change in the pattern as calcined and rehydrated SSZ-51 is dehydrated.

6 Figure 3 is a series of X-ray patterns (synchrotron, 0.704 Angstrom) of as-  
7 made SSZ-51 as it is being calcined. The \* indicates berlinite peaks.

8  
9 DETAILED DESCRIPTION OF THE INVENTION

10  
11 The novel microporous aluminophosphate (or MAPO) of the present invention  
12 can be produced by hydrothermal crystallization from a reaction mixture containing  
13 reactive sources of phosphorus and aluminum and an organic templating agent (4-  
14 dimethylaminopyridine), a source of HF and, optionally, additional divalent metals or  
15 sources of silica. The preparative process typically comprises forming a reaction  
16 mixture which in terms of mole ratios is:

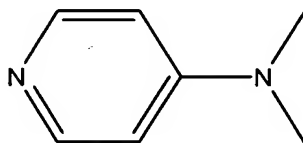


19  
20 where Q is the organic templating agent 4-dimethylaminopyridine. The reaction  
21 mixture is placed in a reaction vessel inert toward the reaction mixture and heated at a  
22 temperature of at least about 100°C, preferably between 100°C and 300°C, until  
23 crystallized, usually a period of from 2 hours to 2 weeks. The solid crystalline  
24 reaction product is then recovered by any convenient method, such as filtration or  
25 centrifugation, washed with water and dried in air at a temperature between ambient  
26 and about 100°C. In a preferred crystallization method, the source of phosphorus is  
27 phosphoric acid, and the source of aluminum is a hydrated aluminum oxide of the  
28 trade name Catapal, the temperature is 150°C to 200°C, the crystallization time is from  
29 2 to 7 days, and the ratio of compounds in the reaction mixture is





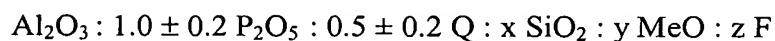
1 The templating agent is 4-dimethylaminopyridine having the structure



3 4-dimethylamino pyridine

4  
5 and is present in the reaction mixture in an amount of from about 0.5 to 0.75 moles  
6 per mole of alumina. Additionally present may be sources of divalent metals such as  
7 magnesium, manganese, cobalt, zinc, nickel and so forth. In these instances it is  
8 anticipated that these metals will replace Al in the lattice so the amount of Al  
9 provided in the synthesis is reduced accordingly. Silica may also be introduced into  
10 the reaction. Typically, silicon will replace P in the lattice, so the amount of P  
11 provided in the synthesis is reduced accordingly.

12 The template-containing as-synthesized form of SSZ-51 has an essential  
13 framework structure whose chemical composition expressed in terms of mole ratios  
14 is:



17  
18 where x, y, Me and z are as defined above. As-synthesized SSZ-51, in an anhydrous  
19 state, has a characteristic X-ray powder diffraction pattern which contains at least the  
20 d-spacings set forth in Table I below.

21  
22 TABLE I  
23 Characteristic peaks of as-synthesized SSZ-51

24

<u>2 Theta<sup>a</sup></u>	<u>d-spacing (Angstroms)</u>	<u>Relative Intensity (%)<sup>b</sup></u>
7.6	11.7	S
8.2	10.8	VS
13.9	6.4	VS
14.1	6.3	S
18.9	4.7	W
19.1	4.6	W-M
19.7	4.5	S
20.0	4.4	W-M
25.8	3.5	S



31.64	2.83	2.7
32.4	2.76	5.3

When the as-synthesized SSZ-51 compositions are calcined, i.e., heated at a temperature sufficiently high, typically between about 300°C and about 700°C, or otherwise treated, such as by chemical oxidation, to remove essentially all of the organic templating agent present in the intracrystalline pore system and then rehydrated, the composition has an X-ray powder diffraction pattern which contains at least the d-spacings set forth in Table II below:

TABLE II  
Characteristic peaks of calcined and hydrated SSZ-51

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Intensity (%)</u>
7.70	11.51	VS
8.08	10.9	VS
13.18	6.7	W
13.80	6.4	W
14.02	6.3	W
16.64	5.32	W
20.20	4.39	M
22.44	3.96	W
23.28	3.82	W
26.62	3.35	M
30.02	2.97	W-M

A complete X-ray powder diffraction pattern (synchrotron, 0.704 Angstrom), including actual relative intensities, for calcined, rehydrated SSZ-51 is set forth in Table IIA below. Intensities were determined by LeBail intensity extraction of the pattern.

TABLE IIA  
Peaks of calcined, rehydrated SSZ-51

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Intensity (%)</u>
3.45	11.7	100
3.63	11.1	63
5.81	6.95	12.2
5.87	6.87	2.7
6.19	6.52	9.9
6.52	6.19	13.2
6.98	5.78	1.3
7.27	5.54	1.9
7.92	5.10	2.3
8.61	4.69	10.7

8.68	4.65	5.7
9.00	4.48	23.2
9.36	4.32	14.8
9.55	4.23	4.6
10.02	4.03	3.1
10.36	3.90	10.2
10.45	3.87	2.1
11.57	3.49	10.9
11.76	3.43	7.4
11.87	3.40	15.6
12.29	3.29	1.9
12.38	3.26	5.0
12.67	3.19	5.9
12.78	3.16	2.9

1

2           The room temperature powder X-ray diffraction pattern of SSZ-51 changes  
3 dramatically after calcination to remove the occluded organic SDA and fluoride ions.  
4 There seems to be a distinct loss of crystallinity, with diffraction peaks for the  
5 calcined sample being much broader and less well defined than for the uncalcined  
6 sample. It would appear that the calcination procedure has probably resulted in some  
7 breakdown of the framework structure. However, calcined SSZ-51 possesses  
8 appreciable microporosity (close to FAU-type molecular sieves), and the density  
9 functional theory (DFT) measurements indicate the likely presence of 12- and 8-rings.  
10 This is consistent with the removal of fluoride and SDA while retaining the  
11 framework structure intact. These two results are therefore seemingly at odds. In order  
12 to follow the calcination process, variable temperature powder X-ray diffraction data  
13 on the as-made sample was collected in order to monitor structural changes as SSZ-51  
14 is heated in air.

15           Figure 3 shows the effect of temperature on the powder diffraction pattern of  
16 the as-made sample of SSZ-51. The data were collected at a synchrotron with a  
17 wavelength of about 0.704 Angstrom with samples in rotating capillaries. Note the  
18 presence of peaks due to berlinite (the AlPO analogue of quartz). As the material is  
19 heated to 300°C, there are only slight changes in the XRD pattern. However, at  
20 400°C there are dramatic changes in both the peak positions and intensities as the  
21 SDA and fluoride are removed from the structure. The shifts are readily apparent in  
22 the positions of the (110), (200), and (310) reflections. This XRD pattern can be  
23 indexed by a C-centered monoclinic cell with lattice parameters of  $a = 22.4$ ,  $b = 13.7$ ,  
24  $c = 14.0$ ,  $\beta = 98.5^\circ$  (as verified by a LeBail profile fit). While the other lattice

1 parameters show little change, the  $a$  lattice parameter increases by 3.3%. This change  
2 seems mostly due to the relaxation of the framework as the fluoride bonds with the  
3 framework are broken.

4 After 400°C, there is little variation in the pattern due to structural changes in  
5 SSZ-51.

6 The good thermal stability of SSZ-51 is quite surprising in that the material  
7 survives calcination to 800°C while retaining a quite crystalline structure. This is at  
8 odds with the room temperature XRD pattern, which shows a distinct loss of  
9 crystallinity. This change in XRD pattern must then be due to the rehydration of the  
10 framework rather than any inherent thermal instability of the framework. On leaving  
11 the calcined SSZ-51 in moist air for a day the broad diffraction pattern of Figure 2 is  
12 again recorded. However, on heating the sample to 100°C, the diffraction pattern  
13 reverts to that which we expect for a highly crystalline sample of SSZ-51, with most  
14 of the expected reflections from the unit cell distinctly visible. It would appear that  
15 the rehydration process affects the crystallinity of the SSZ-51 framework markedly. A  
16 similar effect is seen in the thermal treatment of SAPO-40, which has the related AFR  
17 framework structure described above. Once again, the structure of the framework is  
18 grossly changed by the addition of water at room temperature, removing the long  
19 range order in the structure and producing an X-ray diffraction containing broad  
20 Bragg peaks. In both SSZ-51 and SAPO-40, this behavior is probably closely linked  
21 to the addition of water to the framework aluminum atoms, producing 5- and perhaps  
22 6-coordinated aluminum atoms and so distorting the structure away from that found  
23 for the dehydrated framework.

24 X-ray diffraction data was collected at a synchrotron source with a wavelength  
25 of about 0.704 Angstrom. Interplanar spacings ( $d$ ) in Angstrom units are obtained  
26 from the position of the diffraction peaks expressed as  $2\theta$  (theta) as observed on the  
27 strip chart where theta is the Bragg angle. Intensities were determined from the  
28 heights of diffraction peaks after subtracting background, " $I_0$ " being the intensity of  
29 the strongest line or peak, and " $I$ " being the intensity of each of the other peaks.

30 As will be understood by those skilled in the art the determination of the  
31 parameter  $2\theta$ , irrespective of the technique employed, is subject to both human  
32 and mechanical error, which in combination, can impose an uncertainty of about  $0.1^\circ$   
33 on each reported value of  $2\theta$ . This uncertainty is, of course, also manifested in

1 the reported value of the d-spacings, which are calculated from the 2 theta values.  
2 This imprecision is general throughout the art and is not sufficient to preclude the  
3 differentiation of the present crystalline materials from the compositions of the prior  
4 art. In some of the X-ray patterns reported, the relative intensities of the d-spacings  
5 are indicated by the notations VS, S, M, and W which represent Very Strong, Strong,  
6 Medium, and Weak, respectively.

7 SSZ-51 exhibits surface characteristics which make it useful as a catalyst or  
8 catalyst support in various hydrocarbon conversion and oxidative combustion  
9 processes. SSZ-51 can be associated with catalytically active metals, e.g., by  
10 framework substitution, by impregnation, doping and the like, by methods  
11 traditionally used in the art for the fabrication of catalyst compositions.

12 Further, SSZ-51 has a pore size of less than about 8 Angstroms which makes  
13 SSZ-51 suitable for use as a molecular sieve for the separation of molecular species.  
14 In addition, SSZ-51 is useful in catalysts for hydrocarbon conversion reactions such  
15 as hydrocracking, dewaxing and the like.

#### 16 17 Hydrocarbon Conversion Processes

18 SSZ-51 molecular sieves are useful in hydrocarbon conversion reactions.  
19 Hydrocarbon conversion reactions are chemical and catalytic processes in which  
20 carbon containing compounds are changed to different carbon containing compounds.  
21 Examples of hydrocarbon conversion reactions in which SSZ-51 are expected to be  
22 useful include hydrocracking, dewaxing, catalytic cracking and olefin and aromatics  
23 formation reactions. The catalysts are also expected to be useful in other petroleum  
24 refining and hydrocarbon conversion reactions such as isomerizing n-paraffins and  
25 naphthenes, polymerizing and oligomerizing olefinic or acetylenic compounds such as  
26 isobutylene and butene-1, reforming, isomerizing polyalkyl substituted aromatics  
27 (e.g., m-xylene), and disproportionating aromatics (e.g., toluene) to provide mixtures  
28 of benzene, xylenes and higher methylbenzenes and oxidation reactions. Also  
29 included are rearrangement reactions to make various naphthalene derivatives, and  
30 forming higher molecular weight hydrocarbons from lower molecular weight  
31 hydrocarbons (e.g., methane upgrading).

32 The SSZ-51 catalysts may have high selectivity, and under hydrocarbon conversion  
33 conditions can provide a high percentage of desired products relative to total products.

34 For high catalytic activity, the SSZ-51 molecular sieve should be

1 predominantly in its hydrogen ion form. Generally, the molecular sieve is converted  
2 to its hydrogen form by ammonium exchange followed by calcination. If the  
3 molecular sieve is synthesized with a high enough ratio of SDA cation to sodium ion,  
4 calcination alone may be sufficient. It is preferred that, after calcination, at least 80%  
5 of the cation sites are occupied by hydrogen ions and/or rare earth ions. As used  
6 herein, "predominantly in the hydrogen form" means that, after calcination, at least  
7 80% of the cation sites are occupied by hydrogen ions and/or rare earth ions.

8 SSZ-51 molecular sieves can be used in processing hydrocarbonaceous  
9 feedstocks. Hydrocarbonaceous feedstocks contain carbon compounds and can be  
10 from many different sources, such as virgin petroleum fractions, recycle petroleum  
11 fractions, shale oil, liquefied coal, tar sand oil, synthetic paraffins from NAO,  
12 recycled plastic feedstocks and, in general, can be any carbon containing feedstock  
13 susceptible to zeolitic catalytic reactions. Depending on the type of processing the  
14 hydrocarbonaceous feed is to undergo, the feed can contain metal or be free of metals,  
15 it can also have high or low nitrogen or sulfur impurities. It can be appreciated,  
16 however, that in general processing will be more efficient (and the catalyst more  
17 active) the lower the metal, nitrogen, and sulfur content of the feedstock.

18 The conversion of hydrocarbonaceous feeds can take place in any convenient  
19 mode, for example, in fluidized bed, moving bed, or fixed bed reactors depending on  
20 the types of process desired. The formulation of the catalyst particles will vary  
21 depending on the conversion process and method of operation.

22 Other reactions which can be performed using the catalyst of this invention  
23 containing a metal, e.g., a Group VIII metal such platinum, include  
24 hydrogenation-dehydrogenation reactions, denitrogenation and desulfurization  
25 reactions.

26 The following table indicates typical reaction conditions which may be  
27 employed when using catalysts comprising SSZ-51 in the hydrocarbon conversion  
28 reactions of this invention. Preferred conditions are indicated in parentheses.  
29

Process	Temp., °C	Pressure	LHSV
Hydrocracking	175-485	0.5-350 bar	0.1-30
Dewaxing	200-475 (250-450)	15-3000 psig, 0.103-20.7 Mpa gauge (200-3000, 1.38- 20.7 Mpa gauge)	0.1-20 (0.2-10)
Aromatics formation	400-600 (480-550)	atm.-10 bar	0.1-15
Cat. Cracking	127-885	subatm. <sup>1</sup> (atm.-5 atm.)	0.5-50
Oligomerization	232-649 <sup>2</sup> 10-232 <sup>4</sup> (27-204) <sup>4</sup>	0.1-50 atm. <sup>2,3</sup> - -	0.2-50 <sup>2</sup> 0.05-20 <sup>5</sup> (0.1-10) <sup>5</sup>
Paraffins to aromatics	100-700	0-1000 psig	0.5-40 <sup>5</sup>
Condensation of alcohols	260-538	0.5-1000 psig, 0.00345-6.89 Mpa gauge	0.5-50 <sup>5</sup>
Isomerization	93-538 (204-315)	50-1000 psig, 0.345-6.89 Mpa gauge	1-10 (1-4)
Xylene isomerization	260-593 <sup>2</sup> (315-566) <sup>2</sup> 38-371 <sup>4</sup>	0.5-50 atm. <sup>2</sup> (1-5 atm) <sup>2</sup> 1-200 atm. <sup>4</sup>	0.1-100 <sup>5</sup> (0.5-50) <sup>5</sup> 0.5-50

1

2 <sup>1</sup> Several hundred atmospheres

3 <sup>2</sup> Gas phase reaction

4 <sup>3</sup> Hydrocarbon partial pressure

5 <sup>4</sup> Liquid phase reaction

6 <sup>5</sup> WHSV

7 Other reaction conditions and parameters are provided below.

8



### Hydrocracking

Using a catalyst which comprises SSZ-51, preferably predominantly in the hydrogen form, and a hydrogenation promoter, heavy petroleum residual feedstocks, cyclic stocks and other hydrocrackate charge stocks can be hydrocracked using the process conditions and catalyst components disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753.

The hydrocracking catalysts contain an effective amount of at least one hydrogenation component of the type commonly employed in hydrocracking catalysts. The hydrogenation component is generally selected from the group of hydrogenation catalysts consisting of one or more metals of Group VIB and Group VIII, including the salts, complexes and solutions containing such. The hydrogenation catalyst is preferably selected from the group of metals, salts and complexes thereof of the group consisting of at least one of platinum, palladium, rhodium, iridium, ruthenium and mixtures thereof or the group consisting of at least one of nickel, molybdenum, cobalt, tungsten, titanium, chromium and mixtures thereof. Reference to the catalytically active metal or metals is intended to encompass such metal or metals in the elemental state or in some form such as an oxide, sulfide, halide, carboxylate and the like. The hydrogenation catalyst is present in an effective amount to provide the hydrogenation function of the hydrocracking catalyst, and preferably in the range of from 0.05 to 25% by weight.

### Dewaxing

SSZ-51, preferably predominantly in the hydrogen form, can be used to dewax hydrocarbonaceous feeds by selectively removing straight chain paraffins. Typically, the viscosity index of the dewaxed product is improved (compared to the waxy feed) when the waxy feed is contacted with SSZ-51 under isomerization dewaxing conditions.

The catalytic dewaxing conditions are dependent in large measure on the feed used and upon the desired pour point. Hydrogen is preferably present in the reaction zone during the catalytic dewaxing process. The hydrogen to feed ratio is typically between about 500 and about 30,000 SCF/bbl (standard cubic feet per barrel) (0.089 to 5.34 SCM/liter (standard cubic meters/liter)), preferably about 1000 to about 20,000 SCF/bbl (0.178 to 3.56 SCM/liter). Generally, hydrogen will be separated from the product and recycled to the reaction zone. Typical feedstocks include light

1 gas oil, heavy gas oils and reduced crudes boiling above about 350°F (177°C).

2 A typical dewaxing process is the catalytic dewaxing of a hydrocarbon oil  
3 feedstock boiling above about 350°F (177°C) and containing straight chain and  
4 slightly branched chain hydrocarbons by contacting the hydrocarbon oil feedstock in  
5 the presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi  
6 (0.103-20.7 Mpa) with a catalyst comprising SSZ-51 and at least one Group VIII  
7 metal.

8 The SSZ-51 hydrodewaxing catalyst may optionally contain a hydrogenation  
9 component of the type commonly employed in dewaxing catalysts. See the  
10 aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for  
11 examples of these hydrogenation components.

12 The hydrogenation component is present in an effective amount to provide an  
13 effective hydrodewaxing and hydroisomerization catalyst preferably in the range of  
14 from about 0.05 to 5% by weight. The catalyst may be run in such a mode to increase  
15 isomerization dewaxing at the expense of cracking reactions.

16 The feed may be hydrocracked, followed by dewaxing. This type of two stage  
17 process and typical hydrocracking conditions are described in U.S. Patent  
18 No. 4,921,594, issued May 1, 1990 to Miller, which is incorporated herein by  
19 reference in its entirety.

20 SSZ-51 may also be utilized as a dewaxing catalyst in the form of a layered  
21 catalyst. That is, the catalyst comprises a first layer comprising molecular sieve SSZ-  
22 51 and at least one Group VIII metal, and a second layer comprising an  
23 aluminosilicate molecular sieve which is more shape selective than molecular sieve  
24 SSZ-51. The use of layered catalysts is disclosed in U.S. Patent No. 5,149,421, issued  
25 September 22, 1992 to Miller, which is incorporated by reference herein in its  
26 entirety. The layering may also include a bed of SSZ-51 layered with a non-zeolitic  
27 component designed for either hydrocracking or hydrofinishing.

28 SSZ-51 may also be used to dewax raffinates, including bright stock, under  
29 conditions such as those disclosed in U. S. Patent No. 4,181,598, issued January 1,  
30 1980 to Gillespie et al., which is incorporated by reference herein in its entirety.

31 It is often desirable to use mild hydrogenation (sometimes referred to as  
32 hydrofinishing) to produce more stable dewaxed products. The hydrofinishing step  
33 can be performed either before or after the dewaxing step, and preferably after.

1 Hydrofinishing is typically conducted at temperatures ranging from about 190°C to  
2 about 340°C at pressures from about 400 psig to about 3000 psig (2.76 to 20.7 Mpa  
3 gauge) at space velocities (LHSV) between about 0.1 and 20 and a hydrogen recycle  
4 rate of about 400 to 1500 SCF/bbl (0.071 to 0.27 SCM/liter). The hydrogenation  
5 catalyst employed must be active enough not only to hydrogenate the olefins,  
6 diolefins and color bodies which may be present, but also to reduce the aromatic  
7 content. Suitable hydrogenation catalyst are disclosed in U. S. Patent No. 4,921,594,  
8 issued May 1, 1990 to Miller, which is incorporated by reference herein in its entirety.  
9 The hydrofinishing step is beneficial in preparing an acceptably stable product (e.g., a  
10 lubricating oil) since dewaxed products prepared from hydrocracked stocks tend to be  
11 unstable to air and light and tend to form sludges spontaneously and quickly.  
12 Lube oil may be prepared using SSZ-51. For example, a C<sub>20+</sub> lube oil may be  
13 made by isomerizing a C<sub>20+</sub> olefin feed over a catalyst comprising SSZ-51 in the  
14 hydrogen form and at least one Group VIII metal. Alternatively, the lubricating oil  
15 may be made by hydrocracking in a hydrocracking zone a hydrocarbonaceous  
16 feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically  
17 dewaxing the effluent at a temperature of at least about 400°F (204°C) and at a  
18 pressure of from about 15 psig to about 3000 psig (0.103-20.7 Mpa gauge) in the  
19 presence of added hydrogen gas with a catalyst comprising SSZ-51 in the hydrogen  
20 form and at least one Group VIII metal.

21

#### 22 Aromatics Formation

23 SSZ-51 can be used to convert light straight run naphthas and similar mixtures  
24 to highly aromatic mixtures. Thus, normal and slightly branched chained  
25 hydrocarbons, preferably having a boiling range above about 40°C and less than about  
26 200°C, can be converted to products having a substantial higher octane aromatics  
27 content by contacting the hydrocarbon feed with a catalyst comprising SSZ-51. It is  
28 also possible to convert heavier feeds into BTX or naphthalene derivatives of value  
29 using a catalyst comprising SSZ-51.

30 The conversion catalyst preferably contains a Group VIII metal compound to  
31 have sufficient activity for commercial use. By Group VIII metal compound as used  
32 herein is meant the metal itself or a compound thereof. The Group VIII noble metals  
33 and their compounds, platinum, palladium, and iridium, or combinations thereof can

1 be used. Rhenium or tin or a mixture thereof may also be used in conjunction with  
2 the Group VIII metal compound and preferably a noble metal compound. The most  
3 preferred metal is platinum. The amount of Group VIII metal present in the  
4 conversion catalyst should be within the normal range of use in reforming catalysts,  
5 from about 0.05 to 2.0 weight percent, preferably 0.2 to 0.8 weight percent.

6 It is critical to the selective production of aromatics in useful quantities that  
7 the conversion catalyst be substantially free of acidity, for example, by neutralizing  
8 the molecular sieve with a basic metal, e.g., alkali metal, compound. Methods for  
9 rendering the catalyst free of acidity are known in the art. See the aforementioned  
10 U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a description of such  
11 methods.

12 The preferred alkali metals are sodium, potassium, rubidium and cesium. The  
13 molecular sieve itself can be substantially free of acidity only at very high  
14 silica:alumina mole ratios.

#### 15 16 Catalytic Cracking

17 Hydrocarbon cracking stocks can be catalytically cracked in the absence of  
18 hydrogen using SSZ-51, preferably predominantly in the hydrogen form.

19 When SSZ-51 is used as a catalytic cracking catalyst in the absence of  
20 hydrogen, the catalyst may be employed in conjunction with traditional cracking  
21 catalysts, e.g., any aluminosilicate heretofore employed as a component in cracking  
22 catalysts. Typically, these are large pore, crystalline aluminosilicates. Examples of  
23 these traditional cracking catalysts are disclosed in the aforementioned U.S. Patent  
24 No. 4,910,006 and U.S. Patent No 5,316,753. When a traditional cracking catalyst  
25 (TC) component is employed, the relative weight ratio of the TC to the SSZ-51 is  
26 generally between about 1:10 and about 500:1, desirably between about 1:10 and  
27 about 200:1, preferably between about 1:2 and about 50:1, and most preferably is  
28 between about 1:1 and about 20:1. The novel molecular sieve and/or the traditional  
29 cracking component may be further ion exchanged with rare earth ions to modify  
30 selectivity.

31 The cracking catalysts are typically employed with an inorganic oxide matrix  
32 component. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent  
33 No. 5,316,753 for examples of such matrix components.

## Isomerization

The present catalyst is highly active and highly selective for isomerizing C<sub>4</sub> to C<sub>7</sub> hydrocarbons. The activity means that the catalyst can operate at relatively low temperature which thermodynamically favors highly branched paraffins. Consequently, the catalyst can produce a high octane product. The high selectivity means that a relatively high liquid yield can be achieved when the catalyst is run at a high octane.

The present process comprises contacting the isomerization catalyst, i.e., a catalyst comprising SSZ-51 in the hydrogen form, with a hydrocarbon feed under isomerization conditions. The feed is preferably a light straight run fraction, boiling within the range of 30°F to 250°F (-1°C to 121°C) and preferably from 60°F to 200°F (16°C to 93°C). Preferably, the hydrocarbon feed for the process comprises a substantial amount of C<sub>4</sub> to C<sub>7</sub> normal and slightly branched low octane hydrocarbons, more preferably C<sub>5</sub> and C<sub>6</sub> hydrocarbons.

It is preferable to carry out the isomerization reaction in the presence of hydrogen. Preferably, hydrogen is added to give a hydrogen to hydrocarbon ratio (H<sub>2</sub>/HC) of between 0.5 and 10 H<sub>2</sub>/HC, more preferably between 1 and 8 H<sub>2</sub>/HC. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a further discussion of isomerization process conditions.

A low sulfur feed is especially preferred in the present process. The feed preferably contains less than 10 ppm, more preferably less than 1 ppm, and most preferably less than 0.1 ppm sulfur. In the case of a feed which is not already low in sulfur, acceptable levels can be reached by hydrogenating the feed in a presaturation zone with a hydrogenating catalyst which is resistant to sulfur poisoning. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a further discussion of this hydrodesulfurization process.

It is preferable to limit the nitrogen level and the water content of the feed. Catalysts and processes which are suitable for these purposes are known to those skilled in the art.

After a period of operation, the catalyst can become deactivated by sulfur or coke. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a further discussion of methods of removing this sulfur and coke, and of regenerating the catalyst.

The conversion catalyst preferably contains a Group VIII metal compound to

1 have sufficient activity for commercial use. By Group VIII metal compound as used  
2 herein is meant the metal itself or a compound thereof. The Group VIII noble metals  
3 and their compounds, platinum, palladium, and iridium, or combinations thereof can  
4 be used. Rhenium and tin may also be used in conjunction with the noble metal. The  
5 most preferred metal is platinum. The amount of Group VIII metal present in the  
6 conversion catalyst should be within the normal range of use in isomerizing catalysts,  
7 from about 0.05 to 2.0 weight percent, preferably 0.2 to 0.8 weight percent.

#### 8 9 Alkylation and Transalkylation

10 SSZ-51 can be used in a process for the alkylation or transalkylation of an  
11 aromatic hydrocarbon. The process comprises contacting the aromatic hydrocarbon  
12 with a C<sub>2</sub> to C<sub>16</sub> olefin alkylating agent or a polyalkyl aromatic hydrocarbon  
13 transalkylating agent, under at least partial liquid phase conditions, and in the  
14 presence of a catalyst comprising SSZ-51.

15 SSZ-51 can also be used for removing benzene from gasoline by alkylating the  
16 benzene as described above and removing the alkylated product from the gasoline.

17 For high catalytic activity, the SSZ-51 molecular sieve should be  
18 predominantly in its hydrogen ion form. It is preferred that, after calcination, at least  
19 80% of the cation sites are occupied by hydrogen ions and/or rare earth ions.

20 Examples of suitable aromatic hydrocarbon feedstocks which may be  
21 alkylated or transalkylated by the process of the invention include aromatic  
22 compounds such as benzene, toluene and xylene. The preferred aromatic  
23 hydrocarbon is benzene. There may be occasions where naphthalene or naphthalene  
24 derivatives such as dimethylnaphthalene may be desirable. Mixtures of aromatic  
25 hydrocarbons may also be employed.

26 Suitable olefins for the alkylation of the aromatic hydrocarbon are those  
27 containing 2 to 20, preferably 2 to 4, carbon atoms, such as ethylene, propylene,  
28 butene-1, trans-butene-2 and cis-butene-2, or mixtures thereof. There may be  
29 instances where pentenes are desirable. The preferred olefins are ethylene and  
30 propylene. Longer chain alpha olefins may be used as well.

31 When transalkylation is desired, the transalkylating agent is a polyalkyl  
32 aromatic hydrocarbon containing two or more alkyl groups that each may have from 2  
33 to about 4 carbon atoms. For example, suitable polyalkyl aromatic hydrocarbons  
34 include di-, tri- and tetra-alkyl aromatic hydrocarbons, such as diethylbenzene,

1 triethylbenzene, diethylmethylbenzene (diethyltoluene), di-isopropylbenzene,  
2 di-isopropyltoluene, dibutylbenzene, and the like. Preferred polyalkyl aromatic  
3 hydrocarbons are the dialkyl benzenes. A particularly preferred polyalkyl aromatic  
4 hydrocarbon is di-isopropylbenzene.

5 When alkylation is the process conducted, reaction conditions are as follows.  
6 The aromatic hydrocarbon feed should be present in stoichiometric excess. It is  
7 preferred that molar ratio of aromatics to olefins be greater than four-to-one to prevent  
8 rapid catalyst fouling. The reaction temperature may range from 100°F to 600°F  
9 (38°C to 315°C), preferably 250°F to 450°F (121°C to 232°C). The reaction pressure  
10 should be sufficient to maintain at least a partial liquid phase in order to retard  
11 catalyst fouling. This is typically 50 psig to 1000 psig (0.345 to 6.89 Mpa gauge)  
12 depending on the feedstock and reaction temperature. Contact time may range from  
13 10 seconds to 10 hours, but is usually from 5 minutes to an hour. The weight hourly  
14 space velocity (WHSV), in terms of grams (pounds) of aromatic hydrocarbon and  
15 olefin per gram (pound) of catalyst per hour, is generally within the range of about 0.5  
16 to 50.

17 When transalkylation is the process conducted, the molar ratio of aromatic  
18 hydrocarbon will generally range from about 1:1 to 25:1, and preferably from about  
19 2:1 to 20:1. The reaction temperature may range from about 100°F to 600°F (38°C to  
20 315°C), but it is preferably about 250°F to 450°F (121°C to 232°C). The reaction  
21 pressure should be sufficient to maintain at least a partial liquid phase, typically in the  
22 range of about 50 psig to 1000 psig (0.345 to 6.89 Mpa gauge), preferably 300 psig to  
23 600 psig (2.07 to 4.14 Mpa gauge). The weight hourly space velocity will range from  
24 about 0.1 to 10. U.S. Patent No. 5,082,990 issued on January 21, 1992 to Hsieh, et al.  
25 describes such processes and is incorporated herein by reference.

26 SSZ-51 can also be used to alkylate aromatics compounds using C<sub>20+</sub> olefins.  
27 These alkylated aromatics can then be converted to sulfonic acids or sulfonates and  
28 used as additives in lubricating oils. Such an alkylation process is disclosed in U. S.  
29 Patent No. 5,922,922, issued July 13, 1999 to Harris et al., which is incorporated by  
30 reference in its entirety.

31 The aromatic hydrocarbon that is alkylated in this process is preferably  
32 benzene or toluene, but a higher molecular weight hydrocarbon may also be used.  
33 The feed aromatic hydrocarbon may, therefore be benzene, toluene, xylene,  
34 naphthalene, etc. Preferably it is benzene or toluene, because the resulting alkylates

1 are more easily processed into the corresponding sulfonic acids or LOB or HOB  
2 sulfonates.

3 The olefinic hydrocarbons that are consumed in the process are normal alpha-  
4 olefins (NAO) that may have from about six to thirty carbon atoms per molecule.  
5 Preferably, they have about fourteen to thirty carbon atoms per molecule. Most  
6 preferably, they are predominantly alpha olefins having from twenty to twenty-eight  
7 carbon atoms per molecule.

8 The NAO is isomerized with an acidic catalyst prior to alkylation. Preferably,  
9 the catalyst is a molecular sieve with a one-dimensional pore system such as SM-3,  
10 MAPO-11, SAPO-11, SSZ-32, ZSM-23, MAPO-39, SAPO-39, ZSM-22 and SSZ-20.  
11 Other possible solid acidic catalysts include ZSM-35, SUZ-4, NU-23, NU-87 and,  
12 natural or synthetic ferrierites.

13 The isomerization process conditions are well known in the art. See, for  
14 example, aforementioned U. S. Patent No. 5,922,922.

15 SSZ-51, in acidic form, is used as the alkylation catalyst. Preferably, it is used  
16 predominantly in the hydrogen form.

17 The alkylation process conditions are likewise well known in the art. The  
18 alkylation reaction is typically carried out with an aromatic to olefin mole ratio from  
19 1:15 to 25:1. Process temperatures can range from 100°C to 250°C. As the olefins  
20 have a high boiling point, the process is preferably carried out in the liquid phase.

#### 21 22 Conversion of Paraffins to Aromatics

23 SSZ-51 can be used to convert light gas C<sub>2</sub>-C<sub>6</sub> paraffins to higher molecular  
24 weight hydrocarbons including aromatic compounds. Preferably, the molecular sieve  
25 will contain a catalyst metal or metal oxide wherein said metal is selected from the  
26 group consisting of Groups IB, IIB, VIII and IIIA of the Periodic Table. Preferably,  
27 the metal is gallium, niobium, indium or zinc in the range of from about 0.05 to 5%  
28 by weight.

#### 29 30 Isomerization of Olefins

31 SSZ-51 can be used to isomerize olefins. The feed stream is a hydrocarbon  
32 stream containing at least one C<sub>4-6</sub> olefin, preferably a C<sub>4-6</sub> normal olefin, more  
33 preferably normal butene. Normal butene as used in this specification means all  
34 forms of normal butene, e.g., 1-butene, cis-2-butene, and trans-2-butene. Typically,



1 hydrocarbons other than normal butene or other C<sub>4-6</sub> normal olefins will be present in  
2 the feed stream. These other hydrocarbons may include, e.g., alkanes, other olefins,  
3 aromatics, hydrogen, and inert gases.

4 The feed stream typically may be the effluent from a fluid catalytic cracking  
5 unit or a methyl-tert-butyl ether unit. A fluid catalytic cracking unit effluent typically  
6 contains about 40-60 weight percent normal butenes. A methyl-tert-butyl ether unit  
7 effluent typically contains 40-100 weight percent normal butene. The feed stream  
8 preferably contains at least about 40 weight percent normal butene, more preferably at  
9 least about 65 weight percent normal butene. The terms iso-olefin and methyl  
10 branched iso-olefin may be used interchangeably in this specification.

11 The process is carried out under isomerization conditions. The hydrocarbon  
12 feed is contacted in a vapor phase with a catalyst comprising the SSZ-51. The  
13 process may be carried out generally at a temperature from about 625°F to about  
14 950°F (329-510°C), for butenes, preferably from about 700°F to about 900°F (371-  
15 482°C), and about 350°F to about 650°F (177-343°C) for pentenes and hexenes. The  
16 pressure ranges from subatmospheric to about 200 psig (1.38 Mpa gauge), preferably  
17 from about 15 psig to about 200 psig (0.103 to 1.38 Mpa gauge), and more preferably  
18 from about 1 psig to about 150 psig (0.00689 to 1.03 Mpa gauge).

19 The liquid hourly space velocity during contacting is generally from about 0.1  
20 to about 50 hr<sup>-1</sup>, based on the hydrocarbon feed, preferably from about 0.1 to about  
21 20 hr<sup>-1</sup>, more preferably from about 0.2 to about 10 hr<sup>-1</sup>, most preferably from about 1  
22 to about 5 hr<sup>-1</sup>. A hydrogen/hydrocarbon molar ratio is maintained from about 0 to  
23 about 30 or higher. The hydrogen can be added directly to the feed stream or directly  
24 to the isomerization zone. The reaction is preferably substantially free of water,  
25 typically less than about two weight percent based on the feed. The process can be  
26 carried out in a packed bed reactor, a fixed bed, fluidized bed reactor, or a moving bed  
27 reactor. The bed of the catalyst can move upward or downward. The mole percent  
28 conversion of, e.g., normal butene to iso-butene is at least 10, preferably at least 25,  
29 and more preferably at least 35.

### 30 Xylene Isomerization

31 SSZ-51 may also be useful in a process for isomerizing one or more xylene  
32 isomers in a C<sub>8</sub> aromatic feed to obtain ortho-, meta-, and para-xylene in a ratio  
33

1 approaching the equilibrium value. In particular, xylene isomerization is used in  
2 conjunction with a separate process to manufacture para-xylene. For example, a  
3 portion of the para-xylene in a mixed C<sub>8</sub> aromatics stream may be recovered by  
4 crystallization and centrifugation. The mother liquor from the crystallizer is then  
5 reacted under xylene isomerization conditions to restore ortho-, meta- and  
6 para-xylenes to a near equilibrium ratio. At the same time, part of the ethylbenzene in  
7 the mother liquor is converted to xylenes or to products which are easily separated by  
8 filtration. The isomerate is blended with fresh feed and the combined stream is  
9 distilled to remove heavy and light by-products. The resultant C<sub>8</sub> aromatics stream is  
10 then sent to the crystallizer to repeat the cycle.

11        Optionally, isomerization in the vapor phase is conducted in the presence of  
12 3.0 to 30.0 moles of hydrogen per mole of alkylbenzene (e.g., ethylbenzene). If  
13 hydrogen is used, the catalyst should comprise about 0.1 to 2.0 wt.% of a  
14 hydrogenation/dehydrogenation component selected from Group VIII (of the Periodic  
15 Table) metal component, especially platinum or nickel. By Group VIII metal  
16 component is meant the metals and their compounds such as oxides and sulfides.

17        Optionally, the isomerization feed may contain 10 to 90 wt. of a diluent such  
18 as toluene, trimethylbenzene, naphthenes or paraffins.

19

20

### Oligomerization

21        It is expected that SSZ-51 can also be used to oligomerize straight and  
22 branched chain olefins having from about 2 to 21 and preferably 2-5 carbon atoms.  
23 The oligomers which are the products of the process are medium to heavy olefins  
24 which are useful for both fuels, i.e., gasoline or a gasoline blending stock and  
25 chemicals.

26        The oligomerization process comprises contacting the olefin feedstock in the  
27 gaseous or liquid phase with a catalyst comprising SSZ-51.

28        The molecular sieve can have the original cations associated therewith  
29 replaced by a wide variety of other cations according to techniques well known in the  
30 art. Typical cations would include hydrogen, ammonium and metal cations including  
31 mixtures of the same. Of the replacing metallic cations, particular preference is given  
32 to cations of metals such as rare earth metals, manganese, calcium, as well as metals  
33 of Group II of the Periodic Table, e.g., zinc, and Group VIII of the Periodic Table,  
34 e.g., nickel. One of the prime requisites is that the molecular sieve have a fairly low

1 aromatization activity, i.e., in which the amount of aromatics produced is not more  
2 than about 20% by weight. This is accomplished by using a molecular sieve with  
3 controlled acid activity [alpha value] of from about 0.1 to about 120, preferably from  
4 about 0.1 to about 100, as measured by its ability to crack n-hexane.

5 Alpha values are defined by a standard test known in the art, e.g., as shown in  
6 U.S. Patent No. 3,960,978 issued on June 1, 1976 to Givens et al. which is  
7 incorporated totally herein by reference. If required, such molecular sieves may be  
8 obtained by steaming, by use in a conversion process or by any other method which  
9 may occur to one skilled in this art.

#### 10 Condensation of Alcohols

11 SSZ-51 can be used to condense lower aliphatic alcohols having 1 to  
12 10 carbon atoms to a gasoline boiling point hydrocarbon product comprising mixed  
13 aliphatic and aromatic hydrocarbon. The process disclosed in U.S. Patent  
14 No. 3,894,107, issued July 8, 1975 to Butter et al., describes the process conditions  
15 used in this process, which patent is incorporated totally herein by reference.

16 The catalyst may be in the hydrogen form or may be base exchanged or  
17 impregnated to contain ammonium or a metal cation complement, preferably in the  
18 range of from about 0.05 to 5% by weight. The metal cations that may be present  
19 include any of the metals of the Groups I through VIII of the Periodic Table.  
20 However, in the case of Group IA metals, the cation content should in no case be so  
21 large as to effectively inactivate the catalyst, nor should the exchange be such as to  
22 eliminate all acidity. There may be other processes involving treatment of  
23 oxygenated substrates where a basic catalyst is desired.

#### 24 Methane Upgrading

25 Higher molecular weight hydrocarbons can be formed from lower molecular  
26 weight hydrocarbons by contacting the lower molecular weight hydrocarbon with a  
27 catalyst comprising SSZ-51 and a metal or metal compound capable of converting the  
28 lower molecular weight hydrocarbon to a higher molecular weight hydrocarbon.  
29 Examples of such reactions include the conversion of methane to C<sub>2+</sub> hydrocarbons  
30 such as ethylene or benzene or both. Examples of useful metals and metal  
31 compounds include lanthanide, actinide, molybdenum and/or niobium metals or metal  
32 compounds.  
33

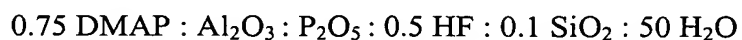
These reactions, the metals or metal compounds employed and the conditions under which they can be run are disclosed in U.S. Patents No. 4,734,537, issued March 29, 1988 to Devries et al.; 4,939,311, issued July 3, 1990 to Washecheck et al.; 4,962,261, issued October 9, 1990 to Abrevaya et al.; 5,095,161, issued March 10, 1992 to Abrevaya et al.; 5,105,044, issued April 14, 1992 to Han et al.; 5,105,046, issued April 14, 1992 to Washecheck; 5,238,898, issued August 24, 1993 to Han et al.; 5,321,185, issued June 14, 1994 to van der Vaart; and 5,336,825, issued August 9, 1994 to Choudhary et al., each of which is incorporated herein by reference in its entirety.

The following examples are provided to illustrate the invention and are not to be construed as limiting thereof:

### EXAMPLE 1

### Synthesis of SSZ-51

SSZ-51 is prepared by combining 1.33 grams of a hydrated aluminum oxide, a pseudo-boehmite phase comprising 75.1 weight percent  $\text{Al}_2\text{O}_3$  and 24.9 weight percent  $\text{H}_2\text{O}$ , with a solution of 2.2 grams of 85 wt % ortho-phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and 9 grams of  $\text{H}_2\text{O}$ . The resulting mixture is stirred until a homogeneous mixture is observed. This mixture is then mixed with 0.22 grams of 50% HF and the resulting mixture stirred until homogeneous. To the above mixture 0.90 grams of 4-dimethylaminopyridine (DMAP) is added and then 0.06 grams of Cabosil M-5 amorphous fumed silica and the resultant mixture is once again mixed until homogeneous. The composition of reaction mixture in molar ratios is:



The reaction mixture is sealed in a stainless steel pressure vessel lined with polytetrafluoroethylene and heated in an oven at 180°C at autogenous pressure for 50 hours. The solid reaction product is recovered by filtration, washed with water and dried in air at ambient temperature.

A portion of the solid reaction product is analyzed and the following chemical analysis obtained:

1.26 wt% Si, 16.21wt% Al, 17.75 wt% P and 1.10 wt% F

The organic content was not obtained in this analysis.

The solid reaction product is analyzed by X-ray powder diffraction and found to be SSZ-51.

## EXAMPLES 2-9

### Synthesis of SSZ-51

In a manner similar to Example 1, SSZ-51 is prepared using the starting materials and conditions shown in Table A below. Elemental analysis for some of the products is shown in Table B below where the numbers are weight percent.

TABLE A

Ex. No.	H <sub>2</sub> O	HF	H <sub>3</sub> PO <sub>4</sub>	Cabosil M-5 or metal	DMAP	Al <sub>2</sub> O <sub>3</sub> <sup>1</sup>	Temp., °C	Time (Days)
2	9 g	0.33 g	2.20 g	0.06 g <sup>2</sup>	0.90 g	1.33 g	180	2.5
3	9 g	0.33 g	2.20 g	0.12 g <sup>2</sup>	0.90 g	1.33 g	180	6
4	9 g	0.22 g	2.0 g	Co <sup>3</sup>	1.20 g	1.33 g	180	2.5
5	9 g	0.33 g	2.2 g	Co <sup>3</sup>	0.90 g	1.20 g	180	2.5
6	9 g	0.22 g	2.2 g	Co <sup>3</sup>	0.90 g	1.26 g	180	2.5
7	9 g	0.22 g	2.2 g	Ni <sup>3</sup>	0.90 g	1.26 g	160	4
8	9 g	0.22 g	2.2 g	Zn <sup>3</sup>	0.90 g	1.26 g	160	4
9	9 g	0.22 g	2.2 g	Mg <sup>3</sup>	0.90 g	1.26 g	160	4

<sup>1</sup> Hydrated aluminum oxide, 75.1 wt.% Al<sub>2</sub>O<sub>3</sub> and 24.9 wt.% H<sub>2</sub>O

<sup>2</sup> Cabosil M-5

<sup>3</sup> 1 mmole added as nitrate salt

TABLE B

Ex. No.	Al	P	Si	Co	F	Ni	Zn	Mg
1	16.1	17.75	1.26		1.10			
5	15.95	19.72		1.91	2.33			
7	14.94	18.79			2.12	3.08		
8	14.57	20.06			1.74		1.73	
9	16.92	20.20			1.46			0.34

## COMPARATIVE EXAMPLE A

A reaction is conducted using the reactants and procedure of Example 1, except that no HF was used. The crystalline product is determined by X-ray analysis to be SAPO-5. This example demonstrates that, when HF is left out of the reaction mixture, SAPO-5 is the product rather than SSZ-51.

## EXAMPLE 10

### Unit Cell from Synchrotron Data

Data is collected on the product of Example 1 with the following experimental parameters: A wavelength of 0.6875 Angstroms (Silicon 111 monochromator) is used in conjunction with Bruker-Nonius goniometer equipped with a 1K CCD area detector and temperature controlled to 150°K. The determination is made that the crystalline solid has, for a monoclinic, C2/c space group the following lattice parameters :

a = 21.759(3) Angstroms

b = 13.8214(18) Angstroms, Beta = 98.849(4) deg.

c = 14.2237 ( 18 ) Angstroms

## EXAMPLE 11

### Calcination of SSZ-51

The material from Example 1 is calcined in the following manner. A thin bed of material is heated in a muffle furnace from room temperature to 120°C at a rate of 1°C per minute and held at 120°C for three hours. The temperature is then ramped up to 540°C at the same rate and held at this temperature for 5 hours, after which it is increased to 594°C and held there for another 5 hours. A 50/50 mixture of air and nitrogen is passed over the SSZ-51 at a rate of 20 standard cubic feet per minute during heating.

## EXAMPLE 12

### Argon Adsorption Analysis

SSZ-51 has a micropore volume (t-plot) of 0.25 cc/gm based on argon adsorption isotherm at 87.3 K recorded on ASAP 2010 equipment from Micromeritics. The low-pressure dose was 2.00 cm<sup>3</sup>/g (STP) with 15-s equilibration interval. The argon adsorption isotherm is analyzed using the density function theory (DFT) formalism and parameters developed for activated carbon slits by Olivier (*Porous Mater.* 1995, 2, 9) using the Saito Foley adaptation of the Horvath-Kawazoe formalism (*Microporous Materials*, 1995, 3, 531) and the conventional t-plot method

1 (J. Catalysis, 1965, 4, 319). The DFT analysis also shows that SSZ-51 has at least one  
2 large pore.

### 3 EXAMPLE 13

#### 4 Calcination of SSZ-51

5 The product of Example 6 is calcined in the manner described in Example 11.

### 6 EXAMPLE 14

#### 7 Constraint Index Determination

8 The hydrogen form of the SSZ-51 of Example 13 is pelletized at 2-3 KPSI,  
9 crushed and meshed to 20-40, and then > 0.50 gram is calcined at about 540°C in air  
10 for four hours and cooled in a desiccator. 0.50 Gram is packed into a 3/8 inch  
11 stainless steel tube with alundum on both sides of the molecular sieve bed. A  
12 Lindburg furnace is used to heat the reactor tube. Helium is introduced into the  
13 reactor tube at 10 cc/min. and at atmospheric pressure. The reactor is heated to about  
14 800°F (427°C), and a 50/50 (w/w) feed of n-hexane and 3-methylpentane is  
15 introduced into the reactor at a rate of 8 µl/min. Feed delivery is made via a Brownlee  
16 pump. Direct sampling into a gas chromatograph begins after 10 minutes of feed  
17 introduction. The Constraint Index value is calculated from the gas chromatographic  
18 data using methods known in the art. SSZ-51 has a Constraint Index of 0.4-0.5 at a  
19 feed conversion of 40% at 800°F (427°C) after 10 minutes. The Constraint-Index  
20 dropped with time on stream. The Constraint Index values over this period continue  
21 to show large pore molecular sieve behavior.

### 22 EXAMPLE 15

#### 23 Hydrocracking of n-Hexadecane

24 A sample of SSZ-51 as prepared in Example 13 is impregnated with  
25 Pd(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> salt using water and giving a 0.5 wt.% Pd value with respect to the  
26 dry weight of the molecular sieve sample. This slurry is stirred for 48 hours at room  
27 temperature. After cooling, the slurry is filtered through a glass frit, washed with  
28 de-ionized water, and dried at 100°C. The catalyst is then calcined slowly up to  
29 482°C (900°F) in air and held there for three hours.

30 The calcined catalyst is pelletized in a Carver Press and crushed to yield  
31 particles with a 20/40 mesh size range. Sized catalyst (0.5 g) is packed into a ¼  
32 inch OD tubing reactor in a micro unit for n-hexadecane hydroconversion.

1           A balance of isomerization and cracking is observed as the catalyst is taken  
2 through a regime of 30% conversion at 600°F (315°C) to 90% at 667°F (353°C). The  
3 cracking increases with temperature. The test is run at a WHSV of 1.55 at 1200 psig  
4 and without titration. Very little C<sub>1</sub> and C<sub>2</sub> are observed and the iso/n ratios for C<sub>4</sub> and  
5 larger are indicative of large pore selectivity.